

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Office



(43) International Publication Date:
October 4, 2001 (04.10.2001)

PCT

(10) International Publication Number:
WO 01/72922 A1

(51) International Patent Classification⁷: C09J 201/02,
115/00, 119/00, 123/26, C08J 3/12, C09J 9/00

Nussloch (DE). **KOHL, Mathias** [DE/DE];
Huntstrasse 8c, 69514 Laudenbach (DE).
FERENCSZ, Andreas [DE/DE];
Kopernikusstrasse 42, 40223 Düsseldorf (DE).

(21) International Application Number:
PCT/EP01/03164

(74) Representative: **MATHES, Nikolaus**; Henkel
Kommanditgesellschaft auf Aktien, Patents
(VTP), 40191 Düsseldorf (DE).

(22) International Filing Date:
March 20, 2001 (20.03.2001)

(81) Designated States (national): CA, JP, US.

(25) Filing Language: German

(84) Designated States (regional): European Patent
(AT, BE, CH, CY, DE, DK, ES, FI, FR, GB,
GR, IE, IT, LU, MC, NL, PT, SE, TR).

(26) Publication Language: German

Published:
— *With an international search report.*
— *Before the expiration of the time limit for
amending the claims and to be republished in
the event of the receipt of amendments.*

(30) Priority Data:
100 15 290.2 March 28, 2000 (28.03.2000) DE

*See the explanations ("Guidance Notes on Codes and
Abbreviations") at the beginning of each regular issue
of the PCT Gazette for an explanation of the two-letter
codes and other abbreviations.*

**(71) Applicant (for all designated states with the exception
of the US):** **HENKEL TEROSON GMBH** [DE/DE];
Hans-Bunte-Strasse 4, 69123 Heidelberg (DE).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **GRIMM, Stefan**
[DE/DE]; Albert-Schweitzer-Strasse 17, 68723
Schwetzingen (DE). **PRÖBSTER, Manfred**
[DE/DE]; Friedrich-Ebert-Strasse 4, 69226

(54) Title: REACTIVE HOT-MELT-TYPE ADHESIVE GRANULATE FOR INSULATING GLASS

(57) Abstract: The invention relates to a reactive batch of thermoplastic polymer particles based on poly- α -olefins, elastomeric block copolymers, and/or polyisobutylenes. Said batch is useful for producing insulating glass units consisting of two or more glass panes, casting resin panes, solar collectors, or facade elements for edifices. The reactive batch contains a portion of batch particles, which contain polymers with reactive groups selected from hydroxyl groups, amino groups, carboxyl groups, carboxylic acid anhydride groups, mercapto groups, silane groups, and/or hydrosilyl groups. Another portion of the batch particles contains polymers with reactive groups that are complementary thereto and are selected from isocyanate groups, epoxy groups, active olefinically unsaturated double bonds, and/or water-producing substances. Said batch of reactive particles is homogenized only directly before the end use and, immediately afterwards, is applied to the substrate surfaces to be joined. Metering problems have not been observed with this type of reactive granulates.

"Reactive Hot-melt Adhesive Granulate for Insulating Glass"

The present invention relates to a reactive batch of thermoplastic polymer particles and to a method for the production of 2- or multi-pane insulating glass.

The 2- or multi-pane insulating glass laminated systems consist of 2 or more parallel glass panes, which are joined at their edge regions in such a manner that the interspace enclosed by the panes is sealed against the surrounding air so that no moisture can penetrate into this interspace.

Furthermore, the edge bond is designed so that it withstands all mechanical and chemical stresses arising due to changing climatic loads. In many cases, this interspace is filled further with dry gases, which increase the thermal insulation or sound insulation compared with normal air filling. Insulating glass of this type is used predominantly in the construction industry, but also in motor vehicle engineering.

The edge bond of such insulating glass can be produced in various ways. In the embodiment still most common today, an aluminum or sheet steel hollow profile is used as a spacer for the desired distance between the glass panes. It is placed near the edges of the glass panes so that the spacer, together with the edge regions of the glass panes, forms an outwardly facing channel for the uptake of sealants and adhesives. These sealants and adhesives effect a sufficiently strong bonding of the insulating glass structure. In high-quality insulating glass systems meeting today's standard, another sealant with a high water-vapor blocking effect is present between the spacer surfaces that face the glass panes, and the glass surface. As a rule, thermoplastic formulations based on polyisobutylene and/or butyl rubber are used for this purpose. The production of such insulating glass structures consists of a series of complex process sequences and is still highly cost-intensive despite a high degree of automation in large production lines. For this reason, attempts have been made to simplify these complex process sequences for the production of insulating glass, whereby particular effort has been made to dispense with preprofiled spacers.

In the so-called "Biver system," for example, a thermoplastic strand, which is preferably based on polyisobutylene or butyl rubber and which may contain a molecular sieve for the adsorption of moisture, is extruded initially onto the edge region of a pane. The second pane is then positioned over it and both panes are then pressed together to the predefined distance. Next, the outer edge region is sealed by a typically 2-component adhesive/sealant. This system has been

described in numerous patents/applications, for example, in DE-C 2555381, DE-A 2555383, DE-A 2555384, and EP-A 176388 or EP-A 714964.

To achieve a force-transmitting coupling of the panes and a dimensionally stable, self-supporting plate-shaped body, WO 94/16187 proposes the use of shaped bodies, made of textile spacer fabric, as spacers between the glass panes. The textile spacer fabric contains highly elastic and flexurally rigid rib fibers and is impregnated with a resin as a binder to create the edge bond. To that end, the edge region of a pane is covered with the resin-impregnated textile spacer fabric. The second pane is then placed over the first pane with an accurate fit and the two panes are pressed together to bond the panes in the edge region. After the press is opened, the reactive binder system can cure.

WO 97/31769 describes the use of a preformed flexible laminate for creating the edge bond of insulating glass panes. This flexible laminate contains, totally or partially embedded within its core material, an undulating sheet material as a spacer, the flat extension of which is perpendicular to the glass panes. The laminate has a polymeric coating on at least one surface that seals the interior of the pane structure from air and/or moisture and maintains the desired distance between the glass panes. To produce laminates of this type, a multistep coextrusion process is necessary, whereby the undulating sheet material is first embedded in a core material, which must then be coated on its outer surfaces with one or several polymeric materials.

According to EP-A 81656, two-pane insulating glass is produced in such a manner that first the edge zones of the glass panes to be bonded are coated with a solution of a primer or adhesive. The glass panes are then brought to the predefined distance and a thermoplastic resin composition consisting of a butyl rubber and a crystalline polyolefin is extruded in the edge region, whereby this thermoplastic composition may also contain tackifiers and drying agents.

A disadvantage of all aforementioned edge bonding systems based on thermoplastic polymers is their low heat resistance and long-term thermal stability. These disadvantages can be overcome only by using reactive systems, such as the reactive hot-melt adhesive, that are either thermally post-cured or post-cured by moisture or oxygen, so that a crosslinked polymer matrix in the edge bond of the insulating glass system provides a sufficient heat resistance. Thus, WO 97/15619 describes sealants/adhesives for the production of insulating glass units based on one-component, hot-applied, chemically curing adhesives/sealants. In this case, these binder systems contain a thermoplastic hot-melt adhesive resin, which is combined with a resin curable by atmospheric

oxygen and/or moisture. In this case, the hot-melt adhesive-resin functions as the meltable component during the initial application and supplies strength immediately upon cooling. The curable polymer phase then begins to react with the oxygen in air or the moisture in air with crosslinking. Moisture-reactive polyurethanes, moisture-reactive polysulfides, polydimethylsiloxanes, or oxygen-cure polysulfides are proposed as curable resins.

The publication DE-A 19821356 describes a process for the production of a silane-modified butyl rubber. Accordingly, a butyl rubber is reacted with a mercapto group-containing silane, which contains hydroxy groups or hydrolyzable groups. This reaction occurs with the aid of a radical former. According to the teaching of this publication, polymers of this type can be combined with other additives in a kneader, processed into a two-component material, and applied to glass with a suitable machine. This applied material then functions simultaneously as a spacer for the two panes; it contains the drying agent for the pane volume and functions as a water-vapor and gas barrier and as an elastic bonded joint.

WO 97/48778 describes a hot-melt adhesive composition containing a mixture consisting of at least one reactive binder based on silane-functional polyisobutylenes, hydrogenated polybutadiene, and/or poly- α -olefins, and a nonreactive binder selected from the group consisting of butyl rubber, poly- α -olefins, polybutenes, styrene block copolymers, or diene polymers. These can be used as a 1- or 2-component adhesive/sealant for the production of insulating glass. Here, no separate spacers made of metal or plastic sections are needed.

In addition to a few processing advantages, the aforementioned different systems have a few disadvantages: in the Biver system, a thermoplastic spacer (Thermoplastic Spacer, TPS) and a conventional, usually two-component adhesive, based on polysulfide, silicone, or polyurethane, are required. With the reactive hot-melt adhesives, in fact only one material is necessary as a rule, but both of the aforementioned binder systems are supplied in drums, from which the material is delivered by pumps to the application site, if necessary after heating. Problems may arise during processing, when with a high material-released quantity per unit time, the melted amount in the material storage compartment of the applicator and the melting rate per unit time are not sufficient to assure the necessary material flow. In addition, in the reactive one-component warm- or hot-melt systems, the problems known to the person skilled in the art occur, such as difficulties in filling, inadequate storage stability, and low full-cure rate, as well as difficulties in the disposal/cleaning of the used, adhesive-contaminated containers.

Proceeding from this state of the art, this invention has as its object the provision of a binder system, which can be applied like the reactive hot-melt adhesives, but which render possible improved storage, conveying, and transport options compared with the state of the art. In particular, the binder system should be easy to handle and especially easy to meter in after long storage as well and with variable temperatures. This includes, furthermore, the avoidance of contamination of transport containers; further, rapid melting and thorough mixing of the reactive components should be possible. Naturally, both the adhesive performance properties and the water-vapor and gas diffusion blocking action should not be negatively affected.

The achievement of the object is to be obtained from the claims. It consists substantially of the provision of a reactive batch of thermoplastic polymer particles based on poly- α -olefins, elastomeric block copolymer, and/or polyisobutylenes, whereby

- a) a portion of these batch particles contains polymers with reactive groups selected from among hydroxyl groups, amino groups, carboxyl groups, carboxylic anhydride groups, mercapto groups, silane groups, and/or hydrosilyl groups and
- b) another portion of the batch particles contains polymers with reactive groups selected from among isocyanate groups, epoxy groups, active olefinically unsaturated double bonds and/or water-containing or water-forming substances, and
- c) optionally another portion of the batch particles contains aids and additives that do not react with the functional groups of the a) and b) particles.

The elastomeric block copolymers within the meaning of this invention include in particular the di- and triblock copolymers of styrene with butadiene or isoprene, as well as the hydrogenation products thereof, e.g., styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), styrene-ethylene-butylene-styrene (SEBS), and styrene-ethylene-propylene-styrene (SEPS).

A further subject of the present invention is a method for the bonding of flat materials, especially insulating glass, which comprises the following essential process steps:

- a) Homogenization and melting of the aforementioned reactive batch, optionally in an inert atmosphere with exclusion of moisture and/or oxygen, whereby a high-shear mixer is used, which can be heated if necessary

- b) Extrusion of the homogenized reactive thermoplastic mixture, optionally by a molding die onto at least one edge region of a sheet material
- c) Subsequent setting of a second sheet material, fitting thereto, onto the applied layer of the reactive mixture
- d) Optionally mechanical fixation and/or pressing together of the assembled sheet materials
- e) Cooling of the thus formed composite system of sheet materials to room temperature, whereby the reactive mixture cures with crosslinking.

A further subject of the present invention is the production of 2-pane or multi-pane insulating glass, cast-resin panes, solar collectors, or facade elements for buildings according to the aforementioned method.

Batch particles within the meaning of this invention are polymer-containing mixtures, which substantially retain their design form at room temperature. Room temperature is to be understood here as a customary storage temperature between 0°C and about 30°C. The granulates in this case have average particle sizes with diameters between 0.5 and 40 mm, preferably between 1 and 30 mm; very especially preferably, the particle size ranges are between particle diameters of 2 and 20 mm. In this case, the particles in principle can have any spatial form desired. This spatial form is determined substantially by the granulate production process. In an especially preferred embodiment, the granulate particles are produced by extrusion through a breaker plate die and the thus extruded strands are cut to the desired length. The granulate core, in this case, may have a spherical form and be disk-shaped, cubic, elliptical, or cylindrical.

The granulate particles thereby contain, in addition to the reactive components according to a) or b), further polyisobutylene, poly- α -olefins, elastomeric block copolymers, waxes, as well as fillers, coloring pigments, and optionally water-binding agents in the form of molecular sieves (drying agents). Furthermore, the granulate particles, especially of component c), can contain additionally aids and additives, such as catalysts, rheological additives, and anti-aging agents, as well as drying agents, dyes, and pigments.

Because of the poly- α -olefin and especially polyisobutylene content, and in part also because of the reactive component content, these granulates, immediately after leaving the extruder or granulator, have a tacky surface that would cause the caking of the granulate particles during

lengthy storage. For this reason, these granulates are customarily surface-coated with a suitable antitack agent immediately after granulation. This antitack agent can consist, for example, of a mixture of talc, pyrogenic silicic acid, and molecular sieve powder. However, other powdered antitack agents can also be used for surface coating. These include carbon black, highly dispersed silicic acid without the other aforementioned ingredients, polyethylene powder, ethylene vinyl acetate powder, or other finely divided polymeric powders. Similarly, antitack agents melting at a slightly elevated temperature, such as, e.g., waxes, can also be sprayed onto the granulate surface. Examples of such waxes are polyolefin waxes, especially polyethylene wax or Fischer-Tropsch wax. The essential selection criterion here is that the particle surface is not tacky at room temperature and at the storage temperature. The end user, however, should be able to incorporate the antitack agent layer into the binder system with no incompatibilities during the further processing. In so doing, this outer, non-tacky layer should surround the core of the granulate so completely that the term continuous surface layer can be used; i.e., as a rule, more than 90%, especially more than 99% of the granulate surface is coated. As a result, the granulate is free-flowing. This means that because of its dead weight, also after rather long storage at temperatures up to 30 or 40°C, it still flows freely through an opening and can thus be conveyed without problems.

Typically, the non-reactive components in the granulate batch particles are present in the following amounts:

poly- α -olefins and/or elastomeric block copolymers 5 to 30% by weight,
polyisobutylene 20 to 50% by weight,
wax 0 to 10% by weight, preferably 0.5 to 5% by weight,
fillers 10 to 30% by weight,
carbon black 5 to 30% by weight, preferably 5 to 20% by weight,
molecular sieve 10 to 20% by weight,
optionally catalysts, rheological additives, anti-aging agents 0.5 to 8% by weight,
reactive polymer 2 to 30% by weight, preferably 5 to 20% by weight.

The non-reactive binders also substantially comprise the group consisting of poly- α -olefins, rubber based on styrene block copolymers with dienes such as, e.g., butadiene or isoprene, whereby these block copolymers may be totally or partially hydrogenated; further, rubber based on random diene-homo- and/or copolymers can be used. Another essential component is butyl rubber in form of polybutenes or polyisobutylenes. Cited as examples from the group of poly- α -

olefins are the ethylene-propylene elastomers, such as, e.g., ethylene-propylene copolymers, and terpolymers of ethylene and propylene with a non-conjugated diene (EPDM) or propylene-butene copolymers, as well as ethylene vinyl acetate.

The rubber based on styrene block copolymers are primarily di- or triblock copolymers of styrene with a diene, such as, e.g., butadiene or isoprene, as can be obtained, e.g., under the trade name "Kraton" from the Shell company. As previously mentioned, these block copolymers can also be used in their hydrogenated or partially hydrogenated form.

Examples of the random diene homo- and copolymers are polybutadiene, polyisoprene, the copolymers thereof, and random styrene-butadiene copolymers (SBR), acrylonitrile-butadiene copolymers (NBR), and the partially hydrogenated or totally hydrogenated diene polymers of the last noted group.

Because of their generally known especially good water-vapor or gas barrier action, the polybutenes and/or polyisobutene, i.e., the polyolefins prepared by stereospecific polymerization of 1-butene or isobutene, and butyl rubber, i.e., copolymers of isobutylene with isoprene, are an especially preferred essential component of the granulate particles.

The reactive thermoplastic polymer granulate particles of the invention contain further ingredients known per se; these include especially water-binding fillers, preferably the zeolites known as molecular sieves of the 3 A-type or calcium oxide in powder form. Furthermore, finely divided inert fillers, such as, e.g., ground or precipitated chalks, kaolin, clays, and carbon black can be used. The chalks, kaolins, or clays can be used thereby both in their form with a hydrophobic surface or also without surface pretreatment.

Furthermore, at least one part of the thermoplastic granulate polymer particles may contain organofunctional silanes as bonding agents and/or crosslinkers; these include, for example, 3-glycidoxypolytrialkoxysilane, 3-acryloxypropyltrialkoxysilane, 3-aminopropyltrialkoxysilane, vinyltrialkoxysilane, N-aminoethyl-3-aminopropyl-dialkoxysilane, vinylaminopropyltrialkoxysilane, or aminoalkyltrialkoxysilane. Methoxy or ethoxy groups are especially preferred thereby as the alkoxy group.

The selection of the anti-aging agents which may be used is determined by the composition of the binders; these can be antioxidants such as sterically hindered phenols, thioethers, or high-molecular-weight mercapto compounds, UV stabilizers such as the known benzotriazoles,

benzophenones, or HALS type compounds (Hindered Amine Light Stabilizer). The addition of known antiozonants can prove to be expedient; in exceptions, the addition of hydrolysis stabilizers may also be necessary.

The reactive components of the thermoplastic granulate particles are thereby polymers or oligomers with reactive groups. The polymers of the group a) and b) can thus be selected from among polymers that bear on average more than one functional group, preferably 2 to 2.5 groups. In this case, these reactive groups for polymers of group a) can be selected from among hydroxyl groups, amino groups, carboxyl groups, carboxylic anhydride groups, mercapto groups, silane groups, and/or hydrosilyl groups.

The reactive groups of the polymers of group b) naturally are to be complementary to the polymers of group a), so that here a 2-component reactive system is latently present. The reactive groups of the polymers of groups b) can thereby be selected from among isocyanate groups, epoxy groups, active olefinically unsaturated double bonds, and/or water-forming substances, or substances that contain water in adsorbed form and can release it.

Specific examples of polymers of group a) are polybutadienes or polyisoprenes with predominantly terminal OH groups, amino groups, carboxyl groups, carboxylic anhydride groups, or mercapto groups, which optionally may be totally or partially hydrogenated. Alkoxysilane group-containing polybutadienes can also be used. Furthermore, silane-functional polyisobutylenes, silane-functional hydrogenated polybutadienes, and/or silane-functional poly- α -olefins, as described in WO 97/48778 on pages 5 to 6, can be used.

An isocyanate-terminated polybutadiene can be used as the reactive polymer and/or oligomer for component b); this is obtained, for example, by reacting OH-group-containing polybutadiene with a diisocyanate, such as, e.g., diphenylmethane diisocyanate (MDI), toluylene diisocyanate (TDI), or similar di- or polyisocyanates well-known from polyurethane chemistry. In the simplest case, the homologue mixture of polynuclear MDI homologues such as the so-called "crude MDI" can also be used in component b). An isocyanate group-containing component b) is thereby combined in a preferable manner naturally with a hydroxyl group-containing or amino group-containing or also mercapto group-containing component a).

In the simplest case, the glycidyl ethers of polyphenols, i.e., the glycidyl ethers of bisphenol A or of novolaks, are an obvious choice as the epoxy group-containing component b). Higher-

molecular-weight epoxy resins obtained by reaction of diglycidyl ethers of bisphenol A, for example, with isocyanate group-containing prepolymers can also be used, however. An epoxy group-containing component b) is preferably combined with an amino group-containing, carboxyl group-containing, carboxylic anhydride group-containing, or mercapto group-containing component a). If component b) contains active olefinically unsaturated double bonds as reactive groups in the polymer, it should be combined with a hydrosilyl group-containing polymer component a). Another option is the combination of highly reactive acrylate or methacrylate polymers of group b) with mercapto group-containing polymers of group a) (so-called "thiol-ene" reaction). The (meth)acrylate polymers of the b) group, however, can also be combined with amino group-containing polymer particles a), which then undergo a Michael addition reaction during crosslinking.

The catalysts to be used in the thermoplastic reactive granulate particles are determined according to the selected reactive system and are known in principle to the person skilled in the art. Examples to be cited here are polyurethane catalysts from the group of the organometallic compounds of tin, iron, titanium, bismuth, aliphatic tertiary amines, and especially cyclic aliphatic amines. Examples of epoxy catalysts here are: tertiary amines, Lewis acids or salts thereof, or complex compounds with organic amines. Furthermore, catalytically active tertiary alkylamines, such as, e.g., tris-(dimethylamino)phenol, piperidine, piperidine derivatives, urea derivatives, or imidazole derivatives can be used as the catalyst for the epoxides. Organometallic compounds, tertiary amines, or acids employed in polyurethane chemistry can be used as crosslinking catalysts for silane group-containing polymers. The catalysts can be added either to the non-reactive component c) or to one of the components a) or b). For example, the polyurethane catalysts can be added to component a), which contains hydroxyl group-, amino group-, or mercapto group-containing polymers.

The individual components a), b), and/or c) are prepared first by homogenizing the mixture components in a kneader, internal mixer, or similar mixer and then extruded in an extruder using suitable equipment—for example, a breaker plate die—and then divided into granulate particles. After the surface coating of these granulate particles with the aforementioned antitack agents, the individual components a), b), and c) are filled in the necessary quantity ratios into storage or transport containers. It may be necessary, for example, with isocyanate group-containing components or silane group-containing components, to seal the containers tightly against moisture after filling. There is a large selection of containers; these can be the customary 200-L

drums, but also large-volume bulk containers or large-volume flexible containers of the so-called "big-bag" type. The only essential requirement is that the suitable storage or transport containers can be sealed tight against moisture, if necessary, and that they make it possible to remove the free-flowing granulates either by gravity or, for example, by pneumatic conveyors.

At the level of the end user, the batches of the invention can then be easily removed from the storage vessel, because they are free-flowing or free-falling and thus can be conveyed to the mixer in a simple manner. Metering problems do not apply here, because the reactive batch particles a) and b) were already blended by the manufacturer in the correct mixing ratio. The mixer must have a high shear, because the granulate particles are broken down in this mixer, optionally with heating, and they form a homogeneous mass, so that the two reactive components a) and b) are combined together. After this homogenization of the thermoplastic melt, it is applied optionally by a molding die to at least one edge region of a sheet material, such as, e.g., a glass plate. The second sheet material is then placed with an accurate fit onto the surface of the extruded reactive thermoplastic material. Next, the two sheet materials are pressed together if necessary and then allowed to cool; the edge bond then immediately has a sufficient initial strength for the other fabrication processes.

The mixture can be heated thereby either by an external heating unit or by the energy introduced by the shear mixing.

Specific examples of such suitable high-shear mixers are one- and multi-screw extruders, kneaders with a discharge screw, and static mixers optionally connected upstream, (co-)kneaders, multi-chamber mixers, or mixers, such as those used in the production of BMC products (bulk molding compound) or special DMC products (dough molding compound), or so-called Conterna mixers (from Ika).

In principle, however, the granulate mixtures of the invention can also be used with small applicators, e.g., conventional cartridges. To that end, these cartridges must be heated if necessary and the piston must be moved by compressed air, hydraulically, or by mechanical drives in order to force the molten granulate out of the cartridge opening. As a high-shear mixer, a static mixer known per se can be connected upstream of a cartridge of this type; static dynamic mixing systems can also be used, as they are disclosed, e.g., in WO 95/24556. Furthermore, static-dynamic mixing systems can be used, as disclosed in EP-A 313519, EP-A 351358, or DE-U 8717424.

The reactive batches of the invention of thermoplastic polymer particles are used preferably for the production of insulating glass, but they can also be used for the production of solar collectors or solar elements. A further field of application is the production of facade elements made of glass and glass-like, plate-like construction components that must be bonded together in the edge region in a force-transmitting/elastic manner. Furthermore, the compositions of the invention can be used for the production of cast-resin panes and for edge sealing in laminated glass.

The invention will be illustrated further using the following exemplary embodiments, whereby the selection of the examples does not represent a restriction of the scope of the subject of the invention. If not stated otherwise, all quantity data in the following examples are percentages by weight or parts by weight based on the total composition.

Examples

In the examples that follow, the formulation components were mixed together until homogeneous in a laboratory kneader under vacuum with exclusion of moisture.

To test the storage stability, a part of this mixture was filled into moisture-tight cans and these were sealed. Even after many weeks of storage in a closed container, the material retained its reactivity and capacity for crosslinking.

To test the full-cure properties, a portion was compressed into disks, 50 mm in diameter and 10 mm thick, and the progress of curing was measured by penetration measurement using the cone penetration method in accordance with ASTM D 217. The cone angle was 30°, weight 150 g, and penetration time 6 seconds. In this respect, the penetration was measured immediately, in the one case, and in others after many days of storage in the standard climate (in accordance with DIN 50014) and at an elevated temperature. The former was used to determine the progress of curing under the environmental conditions, and the latter to determine the accelerated curing.

To determine the tensile strength properties, another portion of the material was compressed into disks, 13 to 14 mm thick, and cut into strips 1 cm wide and 5 cm long. Such strips were placed centrally on a glass plate (dimensions 5 x 5 cm), and a second glass plate was then positioned on the adhesive/sealant strips so that the two glass plates coincided. With the aid of the spacers, the two glass plates were pressed together to a distance of 12.5 mm, so that the adhesive/sealant strips totally moistened both glass plates and had a dimension of 12.5 x 10 x 50 mm. The tensile

strength was then determined using an Instron-type laboratory tensile tester after 1 day of storage of the test pieces at 80°C or several days of storage at 80°C.

Table

Example	1	2	3	4	5	6
Polyisobutylene ¹⁾	145	145	145	145	145	167
Polyethylene wax ²⁾	5	5	5	5	5	5.8
Chalk ³⁾	90	90	90	90	90	103.7
Carbon black ⁴⁾	100	100	100	100	100	115.2
Polybutene-/isobutene ⁵⁾	10	10	10	10	10	11.5
Molecular sieve 3A (powdered)	65	65	65	65	65	74.9
SEBS polymer ⁶⁾		100		100	100	
EB polymer ⁷⁾					20	
Maleinized polybutadiene ⁸⁾	137.4		68.7			
OH-functional polybutadiene ⁹⁾	56		28			
NCO-functional polybutadiene ¹⁰⁾				100	100	115.2
Silane-functional polyisobutylene ¹¹⁾		100				
Polyether plasticizer			6			
GLYMO ¹²⁾		5		5	5	5.76
Potassium octoate			2			
DBTL ¹³⁾				1	1	1.15
Dibutyltin acetylacetone		1.5				
Penetration ¹⁴⁾ (immediate):	93	34	12	19	26	
Penetration (x days NK) ¹⁵⁾	34d-10	63d-20	14d-5	15d-12	12d-17	
Penetration (x days) 80°C	34d-1	63d-8	14d-2	15d-5	12d-6	
Shore A (final value after curing)	80		77			
Tensile value (1 day 80°C) [MPa]		0.5		0.5	0.7	1.2
Tensile value (x days 80°C) [MPa]		50d/0.8		15d/1.5	14d/1.5	14d/1.4

Notes for the Table

- 1) Polyisobutylene, molecular weight about 85,000, penetration 80 (DIN 1995/43), T_g –64°C
- 2) Ethylene homopolymer, drop point 106°C (ASTM D 3954), Brookfield viscosity 350 mPa.s (140°C)
- 3) Precipitated, average particle diameter 0.07 µm, BET surface area 31.6 m²/g, oil absorption value 55
- 4) Printex U, Degussa-Hüls
- 5) MW about 5900, viscosity 40,500 cSt/100 (ASTMD-445)

- 6) 13% styrene portion, 30% diblock portion, about 1% acid anhydride function
- 7) Ethylene-butylene copolymer with terminal OH group (monofunctional)
- 8) Maleic anhydride adduct to 1,4-cis-polybutadiene, molecular weight about 2100, acid number about 88 mg KOH/g
- 9) OH number 46.6, molecular weight about 2800, 60% trans-1,4 double bonds, 20% cis-1,4, 20% vinyl-1,2 double bonds
- 10) Reaction product of TDI and an OH-functional polybutadiene, molecular weight about 3500, 3.1% NCO content
- 11) In accordance with the teaching of EP 758029 or JP 10204222
- 12) Glycidyloxypropyl triethoxysilane
- 13) Dibutyltin laurate
- 14) According to ASTM D 217
- 15) NK = standard climate

The employed molecular sieve had a water content of about 3%.

Example 7

In analogy to Examples 1 to 6, the batch particles for component a) and component b) were prepared separately in a kneader:

Component a)

Polyisobutylene ¹⁾	145 parts
OH-functional polybutadiene ²⁾	100 parts
Chalk ³⁾	90 parts
Carbon black (Printex U) ⁴⁾	100 parts
Molecular sieve 3A (powder)	65 parts
DBTL ⁵⁾	2 parts

Component b)

Polyisobutylene ¹⁾	145 parts
NCO-terminated polybutadiene ⁶⁾	100 parts
Chalk ³⁾	90 parts
Carbon black (Printex U) ⁴⁾	100 parts
Molecular sieve 3A (powder)	65 parts

Examples 8Component a)

Polyisobutylene ¹⁾	145 parts
OH-functional polybutadiene ²⁾	56 parts
Chalk ³⁾	90 parts
Carbon black (Printex U) ⁴⁾	100 parts
Molecular sieve 3A (powder)	65 parts

Component b)

Polyisobutylene ¹⁾	145 parts
Maleinized polybutadiene ⁷⁾	137 parts
Chalk ³⁾	90 parts
Carbon black (Printex U) ⁴⁾	100 parts
Molecular sieve 3A (powder)	65 parts

1) Polyisobutylene, molecular weight about 85,000, penetration 80 (DIN 1995/43), T_g –64°C

2) OH number 46.6, molecular weight about 2800, 60% trans-1,4 double bonds, 20% cis-1,4, 20% vinyl-1,2 double bonds

3) Precipitated, average particle diameter 0.07 mm, BET surface area 31.6 m^2/g , oil absorption value 55

4) Degussa-Hüls

5) Dibutyltin laurate

6) Reaction product of TDI and an OH-functional polybutadiene, molecular weight about 3500, 3.1% NCO content

7) Maleic acid anhydride adduct to 1,4-cis-polybutadiene, molecular weight about 2100, acid number about 88 mg KOH/g

Granulates were prepared from the components a) or b) prepared in Examples 7 and 8 by extrusion of material strands, 8 mm in diameter, and cutting of these strands into 8-mm long pieces; these were then packaged immediately in sealing moisture-tight cans. Even after many weeks of storage, these granulates still exhibited their original reactivity.

For further processing, equal parts of components a) and b) are homogenized and extruded with the appropriate shape. After complete curing of the material, the physical and mechanical data can be determined. The achievable strength values agree largely with those achieved in Examples 1 to 6.

Claims

- 1) Reactive batch of thermoplastic polymer particles based on butyl rubber, elastomeric block copolymers, poly- α -olefins, and/or polyisobutylenes, characterized in that
 - a) a portion of these batch particles contains polymers with reactive groups selected from among hydroxyl groups, amino groups, carboxyl groups, carboxylic anhydride groups, mercapto groups, silane groups, and/or hydrosilyl groups
 - b) another portion contains polymers with reactive groups selected from among isocyanate groups, epoxy groups, active olefinically unsaturated double bonds, and/or water-forming or water-containing substances, and
 - c) optionally another portion of the batch particles contains aids and additives that do not react with the functional polymers of the a) and b) particles.
- 2) Reactive batch according to claim 1, characterized in that the reactive components of the batch portions a) and b) are present in approximately stoichiometric quantity ratios.
- 3) Reactive batch according to claim 1 or 2, characterized in that the aids and additives are selected from catalysts, drying agent, rheology modifiers, anti-aging agents, and/or dyes and pigments.
- 4) Reactive batch according to at least one of the present claims, characterized in that the batch particles of portions a), b), and optionally c) are granulates with average particle sizes of 0.5 to 40 mm, preferably 1 to 30 mm, and especially preferably 2 to 20 mm.
- 5) Reactive batch according to claim 4, characterized in that the particle surface of the granulate particles was treated with tackiness-reducing and/or moisture-binding agents.
- 6) Reactive mixture according to claim 5, characterized in that the tackiness-reducing agents are selected from among finely divided powders in the form of carbon black, highly dispersed silicic acid, polyethylene powder, or talc or consist of sprayable low-melting liquids or liquids that can be applied as powders when in solid form, such as waxes or paraffins.
- 7) Method for bonding sheet materials, characterized by the following essential process steps:
 - a) Homogenization and melting of the reactive batch, according to at least one of claims 1 to 6, optionally in an inert atmosphere with exclusion of moisture and/or oxygen, with use of an optionally heatable high-shear mixer
 - b) Extrusion of the homogenized thermoplastic mixture, optionally by a molding die onto at least one edge region of a sheet material

- c) Setting of a second sheet material, fitting thereto, onto the applied layer of the reactive mixture
 - d) Optionally mechanical fixation of the assembled sheet material
 - e) Cooling of the thus formed composite system to room temperature, whereby the reactive mixture cures with crosslinking.
- 8) Production of 2-pane or multi-pane insulating glass, cast-resin panes, solar collectors, or facade elements for buildings according to a method according to claim 7.